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(54) Title: THERMOSETTING ADHESIVE COMPOSITION, ADHESIVE AND PRODUCTION PROCESS FOR ADHESIVE (57) Abstract The present invention provides a thermosetting adhesive composition that solves the problems of reactive hot melt adhesives of the prior art and that can be used as a heat bonding type adhesive with a high flow resistance during thermocompression bonding and a high soldering heat resistance. The thermosetting adhesive composition comprises an adhesive component containing (a) a polyethylenic copolymer with an epoxy group in the molecule and (b) a rosin, characterized in that the rosin has a carboxyl group in the molecule and the adhesive component further contains an inorganic colloid dispersed therein.		

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THERMOSETTING ADHESIVE COMPOSITION, ADHESIVE AND PRODUCTION PROCESS FOR ADHESIVE

Field of the Invention

5 The present invention relates to an adhesive composition that can be utilized as a reactive (thermosetting) heat bond type adhesive, and particularly it relates to a composition for forming adhesives, which have high flow resistance for thermocompression bonding, which have high soldering heat resistance, and which are suitable for adhesion of electronic parts and fabrication of IC packages.

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Background of the Invention

 In the class of hot melt adhesives that are capable of heat bonding there are known so-called "reactive" (thermosetting) hot melt adhesives that can be subjected to a crosslinking reaction after adhesion for the purpose of improving performance, including heat resistance. Examples of conventional reactive hot melt adhesives include the following types (1) to (6):

- 20 3. Moisture-curing adhesives containing polymers with isocyanate groups (disclosed in U.S. Patent No. 5,418,288 (corresponding Japanese patent application: Japanese Unexamined Patent Publication (Kokai) No. 6-158017));
3. Silanol condensation adhesives containing polymers with silyl groups (disclosed in Japanese Unexamined Patent Publication (Kokai) No. 5-320608);
- 25 3. Radical polymerization adhesives containing polymers with acryloyl groups (disclosed in Japanese Unexamined Patent Publication (Kokai) No. 63-230781);
3. Thermosetting adhesives containing polymers with glycidyl groups and phenol resins (disclosed in Japanese Unexamined Patent Publication (Kokai) No. 6-172731);
- 30 3. A method for crosslinking after heat-bonding by radiation exposure (disclosed in Japanese Unexamined Patent Publication (Kokai) No. 6-306346); and

3. A crosslinking resin composition comprising a terpolymer of ethylene, α , β -unsaturated dicarboxylic acid and α , β -unsaturated dicarboxylic acid ester; ethylene-glycidyl methacrylate copolymer; and a diallyl phthalate compound (disclosed in Japanese Unexamined Patent Publication (Kokai) No. 4-45123).

However, the conventional reactive hot melt adhesives disclosed in these publications still have problems listed below as <1> to <7>:

<1> The crosslinking reactions are generally slow and extended post-curing time is, therefore, necessary (for example in the case of (1) and (2) above);

<2> Moisture is required for the crosslinking reactions, making them unsuitable for adhesion at sections having poor contact with external air (for example in the case of (1) above);

<3> Water is generated as a by-product of the reactions, which may result in adverse effects such as deterioration of adhesive strength over time (for example in the case of (2) above);

<4> Solvents are necessary for molding into film shapes and solvent residues may result in adverse effects after adhesion is complete (for example in the case of (1) to (4) above);

<5> The crosslinking reactions proceed slowly even during common storage at normal temperature (about 25°C), so that the storage stability is lower (for example in the case of (1) to (3) above);

<6> Irradiation-crosslinking type adhesives are unsuitable for sections for which exposure to radiation is impossible or difficult (for example in the case of (5) above); and

<7> Because the thermosetting reaction between the molecules of the copolymer is essential, it is difficult to prevent gelation of the composition by heat during the step of molding into the prescribed shape, such as a film, so that continuous production is substantially impossible (for example in the case of (6) above).

In addition, Japanese Unexamined Patent Publication (Kokai) No. 9-25371 discloses a hot melt adhesive comprising an ethylene-glycidyl methacrylate copolymer as a polyethylenic copolymer, and a rosin. The rosin is added as a

tackifier and works in combination with the polar action of the glycidyl group of the ethylene-glycidyl methacrylate copolymer to provide improved adhesion to metal surfaces. Preferred rosins are rosin esters with acid values of 100 or less. Therefore, this adhesive does not actively utilize the thermosetting reaction
5 between the rosin and the ethylene-glycidyl methacrylate copolymer. Furthermore, this publication does not refer to the crosslinking reaction between the molecules of the ethylene-glycidyl methacrylate copolymer (polyethylenic copolymer).

The aforementioned adhesive containing a polyethylenic copolymer can be suitably used as a hot melt adhesive in the field of electronics. Such polyethylenic
10 hot melt adhesives are chemically stable, and their stability has been demonstrated by testing under harsh conditions, such as the pressure cooker test employed for semiconductor products. When this type of adhesive is used as a film adhesive for attachment of lead pins of an integrated circuit (IC) lead frame, the conditions of use are such that an adhesive tape is thermocompression bonded at a temperature
15 of about 180°C, it is immersed in a soldering bath, and then it is left in a hot environment of 230-260°C. Thus, in order to utilize polyethylenic hot melt adhesives for adhesion of electronic parts and fabrication of IC packages, they must have high flow resistance during thermocompression bonding and high soldering heat resistance. The prior art, however, teaches no specific
20 improvements for satisfying such performance demands.

On the other hand, increasing the reactivity of hot melt adhesives can be advantageous for achieving higher flow resistance during thermocompression bonding and higher soldering heat resistance. However, because reactive hot melt adhesives have the problems listed in <1> to <7> above, they have not been
25 suitable as hot melt adhesives in the field of electronics.

Summary of the Invention

It is therefore an object of the present invention to provide a thermosetting adhesive composition that can solve the aforementioned problems <1> to <7>
30 associated with conventional reactive hot melt adhesives and that has high flow resistance during thermocompression bonding and high soldering heat resistance to allow its use as a heat bonding adhesive.

Detailed Description of the Preferred Embodiments

In order to solve these problems, the present invention provides a thermosetting adhesive composition comprising an adhesive component containing
5 (a) a polyethylenic copolymer with an epoxy group in the molecule and (b) a rosin, characterized in that the rosin has a carboxyl group in the molecule and the adhesive component further contains an inorganic colloid dispersed therein. The thermosetting adhesive composition of the invention overcomes the aforementioned problems of conventional adhesives by the mode described below.

10 The thermosetting adhesive composition of the invention (hereafter sometimes referred to as "adhesive composition") is characterized by containing, as an adhesive component, a polyethylenic copolymer with an epoxy group in the molecule (hereafter sometimes referred to as "copolymer (a)") and a rosin with a carboxyl group in the molecule (hereafter sometimes referred to as "rosin (b)").

15 The thermosetting reaction of the adhesive formed from the thermosetting adhesive composition is substantially a reaction between the "epoxy group" of "copolymer (a)" such as an ethylene-glycidyl (meth)acrylate copolymer and the "carboxyl group" of "rosin (b)". Therefore, no water or other reaction by-products are generated and the crosslinking reaction is generally rapid, so that no extended post-curing is necessary. In addition, no water is necessary for the crosslinking
20 reaction. Solutions to problems <1>, <2>, and <3> are therefore provided.

The adhesive formed from the adhesive composition of the invention is solid at ambient temperature (approximately 25°C; the term "ambient temperature" will hereafter always mean approximately 25°C), and it can be thermocompression
25 bonded at a prescribed temperature and a relatively low pressure in a short time (for example, at 100-200°C, 0.1-10 kg /cm², 0.1-30 seconds) and cured (crosslinked) by heating during compression bonding or heating after compression bonding (post-curing). It is useful as a heat bonding-heat crosslinking adhesive.

Such adhesives can be prepared, for example, by irradiating the adhesive
30 composition with an electron beam to introduce a crosslinked structure between the ethylene units of the polyethylenic copolymer molecules. These adhesives differ from conventional radiation crosslinking adhesives in that their crosslinking can be

completed by heating after the adhesives are applied to sections of adherends whose exposure to radiation is impossible or difficult. The aforementioned problem <6> may, therefore, be solved. The heating temperature for thermosetting is usually 120°C or higher and the heating time is usually one minute or longer.

5 The adhesive composition of the invention can be melted to easily form a hot melt coating at lower temperatures (for example, 120°C or lower) than hot-meltable compositions for common hot melt adhesives. Their fluidity during hot melting is also higher and they require no solvents for coating or molding into film shapes. That is, since they require no solvents for molding of film shapes and,
10 thus, no residual solvent is left after adhesion to produce adverse effects, the problem of <4> above is also solved.

 The curing reaction of copolymer (a) and rosin (b) in the adhesive composition of the invention is extremely moderate at heating temperatures for melt coating or extrusion molding. Hence, there is no gelation of the adhesive
15 composition and its viscosity (complex elastic modulus) does not rise to a level that may cause difficulties for continuous production. In addition, since the curing reaction substantially does not proceed at lower than 90°C, the storage stability of the adhesive composition is increased. The problem of <5> above is, therefore, solved. Furthermore, the composition may be selected so that thermal crosslinking
20 reaction between the molecules of the copolymer is not essential in the crosslinking after application of the adhesive to an adherend (known as after-crosslinking or post-curing), so that gelation of the composition may be effectively prevented during the step of heat molding into the film or other prescribed form, thus facilitating continuous production. The problem of <7> above is, therefore,
25 solved.

 On the other hand, since the curing reaction proceeds rapidly at temperatures of 130°C and above, and especially at 150°C and above, the thermosetting treatment time for postcuring, etc. can be easily shortened.

 The adhesive composition of the invention, in addition to having the
30 thermosetting property described above, is also characterized by further including an inorganic colloid dispersed in the adhesive component. Thus, adhesives formed from the adhesive composition of the invention can be utilized as thermosetting-

heat bonding type adhesives with greater flow resistance during thermocompression bonding and higher soldering heat resistance.

The adhesive of the invention is preferably produced by the following process. Specifically, the adhesive is produced by (i) forming an adhesive composition comprising the adhesive component and the inorganic colloid dispersed in the adhesive component, and (ii) irradiating the adhesive composition with an electron beam to introduce a crosslinked structure between the polyethylenic copolymer molecules included in the adhesive component. This process makes it possible in particular to effectively prevent gelation of the composition in the step of heat molding into a film or other prescribed shape, thus greatly facilitating continuous production.

(Thermosetting adhesive composition)

The thermosetting adhesive composition of the invention preferably contains, in addition to the polyethylenic copolymer with an epoxy group in the molecule (copolymer (a)) and a rosin (b) as the essential adhesive component, also a thermoplastic polymer with no epoxy group in the molecule (c). This helps to increase adhesion of the adhesive (heat bonding film adhesive, etc.) formed from the adhesive composition. Preferred thermoplastic polymers are polyethylenic copolymers (c') with no epoxy groups in their molecules, and particularly preferred are ethylene-alkyl (meth)acrylate copolymers, such as ethylene-ethyl acrylate copolymer. Such polyethylenic copolymers are highly compatible with a polyethylenic copolymer with an epoxy group in the molecule and help to effectively increase thermocompression bonding of the adhesive composition and its melt coating properties without decreasing adhesive properties.

The content of copolymer (a) is usually in the range of 40-98 wt%, and preferably 45-80 wt%, with respect to the total adhesive component weight. The content of the thermoplastic polymer with no epoxy group in the molecule (c), when included, is usually in the range of 1-50 wt%, and preferably 5-20 wt%, with respect to the total adhesive component weight. If the content of the thermoplastic polymer is too low, it is possible that no effect will be obtained, while if the

content of the thermoplastic polymer is too high, it is possible that the reactivity (thermosetting) will be reduced.

The adhesive composition of the invention may also contain other polymers in addition to the aforementioned two types of polyethylenic copolymers, so long
5 as the effect of the invention is not adversely affected.

When heated, the fluidity of the copolymer (a) and the thermoplastic polymer with no epoxy group in the molecule (c) used according to the invention is usually at least 1 [g/10 min] as expressed by the melt flow rate (hereafter sometimes abbreviated to "MFR") measured at 190°C. As long as this value is at
10 least 1, the adhesive composition will be capable of heat bonding. However, in order to facilitate melt coating of the adhesive composition, the value is preferably at least 15. On the other hand, if the MFR is too high, it may reduce the cohesive force of the cured composition. From this viewpoint, the MFR is most preferably in the range of 20-1000. Here, the "MFR" is the value as measured according to
15 JIS K6760. The weight average molecular weight is selected so that the MFR is within the range described above.

The total of copolymer (a) and the thermoplastic polymer with no epoxy group in the molecule (c), which is included if necessary, is normally preferred to be in the range of 60-99 wt% with respect to the total adhesive composition. If the
20 total is too small, it is possible that the adhesion will be reduced.

(Thermosetting adhesive)

The adhesive composition of the invention is suitable as an adhesive precursor composition for the production of thermosetting adhesives. An adhesive
25 according to the invention is preferably made by using the aforementioned adhesive composition and introducing a crosslinked structure between the ethylene units of the polyethylenic copolymer molecules in the adhesive component. Such a crosslinked structure is employed to improve the elastic modulus of the adhesive during thermocompression bonding. Improvement in the elastic modulus will
30 prevent unnecessary excess flow of the adhesive layer sandwiched between two adherends during the thermocompression bonding operation, and thus effectively

prevents seepage of the adhesive from between the adherends with a resulting loss of thickness of the adhesive layer that can reduce its adhesion performance.

The elastic modulus of the adhesive, which affects the performance in this way, is preferably defined by the storage elastic modulus (G') at 250°C. However, since an adhesive according to the invention undergoes an accelerated curing reaction upon heating, a constant elastic modulus will usually not be exhibited at this temperature. The storage elastic modulus of the adhesive is, therefore, defined in the following manner. That is, it is defined as the value obtained at 250°C by using an unused sample of the adhesive (before thermocompression bonding, etc. and before application to an adherend), increasing the temperature of the sample from 90°C to 300°C at a temperature-elevating rate of 5°C/min at a shear rate of 6.28 rad/sec using a dynamic viscoelastic measuring apparatus.

The storage elastic modulus of the adhesive according to this definition is usually in the range of 1×10^4 to 1×10^7 Pa, and preferably 2×10^4 to 1×10^6 Pa. If the storage elastic modulus is too small, the effect of preventing flow during the thermocompression bonding operation will be reduced. If it is too large, there will be a risk of poor adhesion (temporary adhesion) in procedures involving instant thermocompression bonding (for example, up to 30 seconds). Poor temporary adhesion will result in separation of adhesive-attached parts from their base when those parts are transported to later steps (such as a post-curing step).

The intermolecular crosslink is usually formed between ethylene units of the molecules of copolymer (a). When a "polyethylenic copolymer (c') with no epoxy group in the molecule (c') (hereafter sometimes referred to as "copolymer (c')") such as ethylene-alkyl (meth)acrylate copolymer or the like, is included in the composition as an additional component, the crosslink is formed between ethylene units of the molecules of copolymer (c'), molecules of copolymer (a), or molecules of copolymer (c') and copolymer (a). Such intermolecular crosslinking proceeds through a crosslinking reaction between ethylene units upon radical activation of the ethylene units of copolymer (a) and/or (c') by, for example, electron beam radiation.

The adhesive of the invention may be produced by forming the adhesive composition into a film or other shape, irradiating the resulting form with an

electron beam to create a crosslinked structure between molecules of the copolymer. For example, it may be produced by the following process. First, the polyethylenic copolymer with an epoxy group in the molecule (copolymer (a)) is mixed together with the inorganic colloid to make a master batch. The master batch is usually formed into pellets to facilitate subsequent kneading steps. The master batch may also be prepared using the entire amount of copolymer (a) to be included in the final adhesive composition, but generally only a portion of this amount of copolymer (a) is used. Next, the master batch pellets with the remaining amount of copolymer (a) are charged from the initial zone of the extruder, and kneaded and then the hot melted rosin (b) is added from a subsequent zone, so that an adhesive composition as a uniform mixture of all of the components is obtained from the final outlet. If a thermoplastic polymer with no epoxy group in the molecule (c), such as copolymer (c'), is added to the composition, it is usually charged with the other components from the initial zone.

The adhesive composition obtained in this manner is used to form a film by T-die coating or another coating method, and the formed film is irradiated with an electron beam to introduce a crosslinked structure between molecules of copolymer (a) and/or (c'), thus producing a film-like adhesive according to the invention.

20

(Polyethylenic copolymer with an epoxy group in the molecule)

The polyethylenic copolymer with an epoxy group in the molecule (copolymer (a)) may be, for example, polyethyleneglycidyl (meth)acrylate copolymer. When the adhesive composition is heated at a prescribed temperature, copolymer (a) undergoes a curing reaction with rosin (b), acting to increase the cohesive force of the cured product. A high cohesive force is advantageous for improving adhesive performance of the adhesive composition. Electron beam irradiation also creates a crosslinked structure between the molecules of copolymer (a) and/or the molecules of copolymer (c'), thus acting to improve the elastic modulus of the adhesive composition during thermocompression bonding. On the other hand, it also causes relatively low temperature melting of the adhesive composition, thus facilitating melt coating. It also provides the adhesive

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composition with satisfactory thermal adhesive properties (i.e., the adhesive properties on adherends after melting, bonding to the adherends and cooling to solidification.)

The copolymer (a) may be obtained, for example, by polymerization using a monomer mixture comprising: (i) glycidyl (meth)acrylate monomer, and (ii) ethylene monomer as starting monomers. Propylene, alkyl (meth)acrylate, vinyl acetate or the like may also be used as an additional third monomer, so long as the effect of the invention is not prevented. In such cases, the carbon number of the alkyl group of the alkyl (meth)acrylate is usually in the range of 1 to 8.

As specific examples of copolymer (a) there may be mentioned:

- 1: glycidyl (meth)acrylate and ethylene bipolymer,
- 2: glycidyl (meth)acrylate, vinyl acetate and ethylene terpolymer, and
- 3: glycidyl (meth)acrylate, ethylene and alkyl (meth)acrylate terpolymer.

These types of copolymers (a) contain the repeating unit resulting from

polymerization of the monomer mixture comprising glycidyl (meth)acrylate and ethylene, in an amount of usually at least 50 wt% and preferably at least 75 wt%, with respect to the total polymer. Also, the polymerization ratio (G:E) of glycidyl (meth)acrylate (G) and ethylene (E) in the repeating units is preferably in the range of 50:50-1:99, and more preferably 20:80-5:95. If the ethylene content is too low, the compatibility of copolymer (a) with copolymer (c) and rosin (b) will be reduced. As a result, the resulting composition may not be uniform, and electron beam crosslinking may also be more difficult. Conversely, if the ethylene content is too high, the adhesive performance may be reduced. Copolymer (a) may be used as a single type or a mixture of two or more types.

(Thermoplastic polymer with no epoxy group in the molecule)

The thermoplastic polymer with no epoxy group in the molecule ©, which is included in the adhesive composition of the invention when necessary, is preferably a polyethylenic copolymer (c'). Copolymer (c') has the effect of allowing the adhesive composition to be melted at a relatively low temperature, facilitating the melt coating, and increasing the heat bonding of the adhesive composition. Electron beam irradiation forms a crosslinking structure between the

molecules of copolymer (c') and/or the molecules of copolymer (a), thus improving the elastic modulus during thermocompression bonding of the adhesive composition. In addition, since copolymer (c') has lower moisture absorption than copolymer (a), it also serves to increase the water resistance of the adhesive composition. Also, because its softening point is lower than that of copolymer (a), it has the function of alleviating internal stress during the heat cycle of the cured composition, and thus enhancing the adhesive performance.

Ethylene-alkyl (meth)acrylate copolymer is preferably used as copolymer (c'). This copolymer can be obtained by polymerizing a monomer mixture comprising:

3. alkyl (meth)acrylate monomer, and (b) ethylene monomer as the starting monomers. Propylene, vinyl acetate or the like may also be used as an additional third monomer, so long as the effect of the invention is not prevented. The starting monomers for the ethylene-alkyl (meth)acrylate copolymer do not include copolymerizable monomers with epoxy groups. The starting monomers may include copolymerizable monomers with carboxyl or carboxylic anhydrous functional groups so long as the effect of the invention is not prevented, but it is preferred for such functional groups to be substantially absent. This will avoid a heat curing reaction between copolymer (a) and copolymer (c') and thus help considerably in preventing gelation and undesirable viscosity increase of the composition during the molding step into a film or other shape.

The number of carbon atoms of the alkyl group of the alkyl (meth)acrylate in the ethylene-alkyl (meth)acrylate copolymer is preferably in the range of 1 to 4. If the number of carbon atoms of the alkyl group is greater than 4, it may become difficult to increase the elastic modulus of the composition after crosslinking.

As specific ethylene-alkyl (meth)acrylate copolymers there may be mentioned

1: alkyl (meth)acrylate and ethylene bipolymers, and

2: alkyl (meth)acrylate, vinyl acetate and ethylene terpolymers.

These types of copolymers contain a repeating unit resulting from polymerization of a monomer mixture comprising alkyl (meth)acrylate and ethylene, in an amount

of usually at least 50 wt% and preferably at least 75 wt%, with respect to the total polymer. Also, the polymerization ratio (A:E) of alkyl (meth)acrylate (A) and ethylene (E) in the repeating units is preferably in the range of 60:40-1:99, and more preferably 50:50-5:95. If the ethylene content is too low, the enhancing effect on the elastic modulus by electron beam crosslinking may be reduced, while if the ethylene content is too high, the adhesive performance may be reduced. Copolymer (c') may be used as a single type or a mixture of two or more types.

(Rosin with carboxylic group in the molecule (rosin (b)))

The rosin used in the invention (hereafter sometimes referred to as "rosin (b)") has a carboxylic group and it reacts with copolymer (a) during the thermosetting process for heat curing of the adhesive composition, thus serving to increase the adhesive performance.

Rosin (b) may be gum rosin, wood rosin or tall oil rosin, which may also be in a chemically modified form (such as a polymerized rosin). The acid value of rosin (b) is preferably 100-300, and especially 150-250. If the acid value is too low, reactivity with copolymer (a) may be lowered, thus reducing curability of the composition. If it is too high, stability during heat molding (viscosity controlling effect) may be decreased. Here, the "acid value" is the mg value of the mass of potassium hydroxide required to neutralize 1 g of the sample.

The softening point of rosin (b) is preferably 50-200°C, and more preferably 70-150°C. If the softening point is too low, reaction may occur with copolymer (a) during storage, thus decreasing the storage stability. If it is too high, reactivity with copolymer (a) will be lowered, which may reduce the curability of the composition. Here, the "softening point" is the value as measured according to JIS K6730.

The proportion of rosin (b) contained in the adhesive component of the invention is usually 1-20 wt%. At less than 1 wt% curability and heat bonding properties of the composition may be reduced. A greater than 20 wt%, adhesive performance of the composition after curing may be impaired. From this viewpoint, it is preferably within a range of 2-15 wt%, and more preferably 3-10 wt%.

Rosin (b) may be used as a single type or a mixture of two or more types. It may also be used in combination with a rosin containing substantially no carboxylic groups, so long as the effect of the invention is not prevented.

5 **(Inorganic colloid)**

The inorganic colloid is usually present in a dispersion in the form of colloidal particles. The dispersion is stable, with no precipitation of the particles by gravity. Thus, with an adhesive composition according to the invention that is formed by drying such a dispersion, it is possible to achieve a uniform mixture of
10 each of the components, thus especially facilitating increased flow resistance during thermocompression bonding and higher soldering heat resistance.

The content of the inorganic colloid is not particularly restricted so long as the effect of the invention is not prevented, but it is normally 1-40 wt% with respect to the total volume of the adhesive composition. At less than 1 wt%, the
15 dimensional stability may be impaired. A greater than 40 wt%, the peel adhesive strength may be reduced. From this viewpoint, the preferred content is in the range of 2-30 wt% with respect to the total volume of the adhesive composition.

Here, "inorganic colloid" refers to fine particles with an average particle size usually in the range of 1-100 nm. For example, an inorganic particle sol may
20 be mixed with an adhesive component for dispersion in the adhesive component. The inorganic particle sol is usually a mixture of (i) a dispersion medium and (ii) the inorganic colloid dispersed in the dispersion medium.

Silica colloid is preferred as the inorganic colloid. It is particularly effective for increasing the flow resistance and soldering heat resistance during
25 thermocompression bonding.

The inorganic colloid is preferably one which has been subjected to surface treatment with a surface treatment agent. This can effectively enhance the soldering heat resistance and improve the flowability (increase the flow resistance) of the adhesive during thermocompression bonding.

30 A surface modifier, for example an organic silicon compound or an organic titanate compound, may be used as the surface treatment agent. Suitable organic silicon compounds include alkylchlorosilanes, alkylalkoxysilanes,

polydimethylsiloxane, alkylidisilazones, aminosilane, thiolsilane, epoxysilane and ureasilane. These organic silicon compounds may be used alone or in any desired combination of two or more.

5 Particularly preferred are alkylidisilazones. They have particularly excellent soldering heat resistance, and can give adhesives which pass level 1, the highest level of the soldering heat resistance standards of the JEDEC (Joint Electron Device Engineering Council, Japan).

10 The surface treatment of the inorganic colloid is usually carried out by adding the surface treatment agent to a dispersion of the particles and extending the dispersion process. The surface treated dispersion may be utilized as a sol containing the surface treated colloid particles. After drying the dispersion, it may also be subjected to crushing, if necessary, to obtain the particles as a surface treated powder. The amount of the surface treatment agent is usually 0.001-30 parts by weight to 100 parts by weight of the inorganic colloid.

15 (Film adhesive)

A film adhesive comprising an adhesive according to the invention is useful as a heat bonding type adhesive material and it can overcome the problems associated with conventional hot melt adhesives, as described above. The film adhesive is suitable for thermocompression bonding by, for example, insertion
20 between two adherends and subjection to thermocompression bonding at a prescribed temperature and more excellent adhesive performance may be achieved by further post-curing treatment at a prescribed temperature for a prescribed period of time.

The curing reaction proceeds at a temperature of 120°C or higher and
25 heating for a period of between one minute and 24 hours (heating during compression bonding or post-curing) can provide sufficient adhesive strength (for example, 4-15 kg/25 mm or greater). Although the curing reaction rate is moderate at a temperature of 120°C, the desired adhesive performance can be achieved if sufficient time is allowed (for example, 10 hours or longer). The curing time can
30 also be shortened by heating within a range of 130-300°C.

A film adhesive may be produced, for example, in the following manner. First, an adhesive composition according to the invention is prepared containing

each of the aforementioned components. The adhesive composition is then melt coated onto a substrate such as release paper (liner) to form a film-like adhesive composition. Finally, the film like adhesive composition is irradiated with an electron beam to form a crosslinked structure between the molecules of the ethylene unit-containing copolymer, to fabricate a film adhesive comprising an adhesive according to the invention.

The adhesive composition is usually prepared by combining the components of the starting material in a substantially uniform manner using a kneading or mixing apparatus. The apparatus used may be a kneader, roll mill, extruder, planetary mixer, homomixer or the like. The mixing temperature and time are selected so as to substantially prevent reaction between copolymer (a) and rosin (c), usually for a temperature in the range of 20-120°C and a time in the range of one minute to 2 hours.

The complex elastic modulus η^* of the adhesive composition as measured under conditions of 120°C, 6.28 rad/sec is preferably in the range of 500-1,000,000 poise, and more preferably 1,200-10,000 poise. If the complex elastic modulus η^* is too low, molding (or coating) to the desired thickness may become difficult. If it is too high, it may become difficult to accomplish continuous molding.

The melt coating is usually carried out at a temperature in the range of 60-120°C. Common applicator means, such as a knife coater, die coater, etc. may be employed for the coating. A film-like adhesive composition may also be formed by extrusion without using a substrate. The electron beam irradiation is usually carried out using an electron beam accelerator at an acceleration voltage in the range of 150-500 kV and an irradiation dose in the range of 10-400 kGy.

One or both of the adhesive sides of the film adhesive are usually protected with a liner to prepare a product. For adhesive sides with relatively low adhesion, it may be possible to prepare the product without providing a liner.

The thickness of the film adhesive is preferably in the range of 0.001-5 mm, and more preferably 0.005-0.5 mm. If the thickness is too small, the film adhesive will tend to be more difficult to manage. If it is too large, crosslinking will not occur uniformly across the thickness, which may lower reliability of the adhesive.

Liner-attached film adhesives obtained as described above may be used in the following manner, for example. First, the liner is removed from the liner-attached film adhesive, and the adhesive film is sandwiched between a first adherend and a second adherend to form a laminate with the first adherend, film adhesive, and second adherend in this order. Next, the laminate is subjected to thermocompression bonding at a temperature in the range of 80-300°C and a pressure in the range of 0.1-100 kg /cm², to form an adhesive structure with the three layers attached together. This process allows two adherends to be attached with adequate adhesive strength in a time of between 0.1-30 seconds.

An adhesive film according to the invention will naturally exhibit adequate adhesive strength with only the thermocompression bonding described above, but post-curing may also be carried out for increased adhesive strength. Specifically, for the aforementioned adhesion process, post-curing of the adhesive structure is usually carried out at a temperature of 120°C or higher, preferably in the range of 130-300°C, for a time of from one minute to 24 hours. Particularly preferred conditions for a shorter post-curing step are 140-200°C for 30 minutes to 1.2 hours. This process is one preferred embodiment of an adhesion process using a film adhesive according to the invention. Alternatively, instead of preparing a film adhesive, the surface of the first or second adherend may be directly coated with the adhesive composition and irradiated with an electron beam to form an adhesive composition layer to give the adhesive structure described above.

(Other materials)

The adhesive material of the invention may also contain various other additives in addition to the adhesive components (a)-(c) and an inorganic colloid, so long as the effect of the invention is not prevented. Such additives include antioxidants, ultraviolet absorbers, fillers other than inorganic colloids (polymer particles, electroconductive particles, pigments, etc.), waxes and other lubricants, rubber components, tackifiers, crosslinking agents and curing accelerators.

(Uses)

The adhesive composition or adhesive of the invention may be very suitably employed for adhesive of electronic parts, such as adhesion between IC

parts and printed circuit boards. It may also be suitably used for adhesion between polymer adherends made of fluorinated polymers, polyamides, polyimides, polyether imides, polycarbonates, polyethylene, polypropylene, polyester, epoxy resins, etc., or between polymer adherends and objects made of other materials (fibers, metals, silicon semiconductors, ceramics, glass, etc.). As examples of specific metals there may be mentioned copper, iron, nickel, gold, silver, aluminum, tungsten, molybdenum and platinum.

The adhesive composition or adhesive of the invention may be thermocompression bonded at a relatively low temperature and can provide sufficient adhesive strength with post-curing alone at a relatively low temperature and short curing time. It is, therefore, suitable for adhesion of adherends with relatively low heat resistance.

In addition, in the production of the invention, a copolymer (a) and optional copolymer (c) may be ones that have been refined to remove residual contaminants such as unreactive monomers. Therefore, production of the adhesive composition of the invention does not require a polymerization step using monomers as the starting material. It is, therefore, possible to minimize residual by-products in the adhesive, such as unreacted monomers and monomer-derived volatile organic substances. Specifically, it is possible to effectively prevent foaming of volatile components produced during solder reflow and generation of monomer odors that are disagreeable to users.

The adhesive composition of the invention can be used as a thermocompression bonding adhesive tape if it is attached as an adhesive layer to a polymer film, fiber fabric, metal foil or other substrate. The adhesive composition of the invention may also be used as a sealing material instead of an adhesive.

Examples

(Examples 1-5 and Comparative Examples 1-4)

Portions of the amounts of ethylene-glycidyl methacrylate copolymer (copolymer (a): product name: "Bondfast CG5001" by Sumitomo Chemical Co.; MFR = 350 g/10 min, ethylene unit:glycidyl methacrylate unit = 82:18 (weight proportion)) for each of the examples were kneaded with the silica colloids listed

in Table 1 to manufacture master batch pellets. These master batch pellets were then introduced and kneaded with the remaining ethylene-glycidyl methacrylate and ethylene-ethyl acrylate (copolymer (c')) at the initial zone of an extruder, while a hot-melted rosin (b) was added at an intermediate zone, to obtain adhesive compositions according to each of Examples 1-5 from the final outlet, as uniform mixtures of all of the components. This kneading procedure was carried out at a temperature of 110°C.

The proportion of each of the components (all in units of parts by weight) in the adhesive compositions of the examples are listed in Table 1. The product names and suppliers are also listed in Table 1.

In addition, an adhesive composition was prepared for Comparative Example 1 in the same manner as Example 1, except that no silica colloid was used. Also, adhesive compositions were prepared for Comparative Examples 2-4 in the same manner as Example 1, except that fine particles with a relatively large particle size (100 microns or larger) were used instead of the silica colloid.

Each of the adhesive compositions for the examples obtained in the manner described above was hot melt coated using a T-die coater and molded into a film shape, and the molded film was irradiated with an electron beam to introduce a crosslinked structure between the molecules of the ethylenic copolymer in order to obtain a film adhesive for each of the examples. The thickness of the film adhesive was 100 microns. The conditions for the electron beam irradiation were 200 kV, 150 Kgy.

Table 1

	Composition of adhesive component CG5001/KE604/NUC6070/NUC6570	Inorganic colloid
Example 1	70/5/8/17	SY1 = 8
Example 2	70/5/8/17	SI1 = 8
Example 3	70/5/8/17	SA1 = 8
Example 4	70/5/8/17	SX1 = 8
Example 5	70/5/8/17	SH1 = 8
Comp. Ex. 1	70/5/8/17	none
Comp. Ex. 2	77/5/8/17	TA2 = 11
Comp. Ex. 3	75/5/8/17	LA2 = 7
Comp. Ex. 4	82/5/8/17	BA2 = 7

Note 1: All units are parts by weight.

Note 2:

- 5 CG5001: Ethylene-glycidyl methacrylate copolymer, product name: Bondfast, Sumitomo Chemical Co.
- KE604: Rosin, product name: Paine crystal, Arakawa Chemistry, acid value = 242
- 10 NUC6070: Ethylene-ethyl acrylate copolymer, Nippon Unicar Co., Ltd., MFR = 250 g/10 min, ethylene unit:ethyl acrylate unit = 75:25
- NUC6570: Ethylene-ethyl acrylate copolymer, Nippon Unicar Co., Ltd., MFR = 20 g/10 min, ethylene unit:ethyl acrylate unit = 75:25
- SY1: Silica colloid, RY200, Nippon Aerosil Co., Ltd., mean particle size = 12 nm (surface treatment agent = polydimethylsiloxane)
- 15 SI1: Silica colloid, R974, Nippon Aerosil Co., Ltd., mean particle size = 12 nm (surface treatment agent = dimethyldichlorosiloxane)
- SA1: Silica colloid, 200, Nippon Aerosil Co., Ltd., mean particle size = 12 nm (untreated)
- SX1: Silica colloid, RX974, Nippon Aerosil Co., Ltd., mean particle size = 12
- 20 nm (surface treatment agent = hexamethyldisilazane)
- SH1: Silica colloid, R805, Nippon Aerosil Co., Ltd., mean particle size = 12 nm (surface treatment agent = octyltriethoxysilane)
- TA2: Fine particulate titanium oxide, MT-500HD, Tayka Corporation, mean particle size = 1.7 μ m
- 25 LA2: Talc, FFR, Asada Milling Co., Ltd., mean particles size = 3.6 μ m

BA2: Precipitated barium sulfate, #300, Sakai Chemical Industries Co., Ltd.,
mean particle size = 0.77 μm .

The examples were evaluated in the following manner.

5 3. Flow Property (Flow Resistance)

A film adhesive with a 6 mm diameter and 0.1 mm thickness was
thermocompression bonded at 180°C and 90 kg/cm² for 10 seconds. The post-
compression diameter percentage with respect to the pre-compression diameter (=
[post-compression diameter/pre-compression diameter] x 100) was defined as the
10 flow property [%]. Samples having relatively low flow resistance with a flow
property over 220% in this test were judged as "NG" (failure to match required
standard) and those having relatively high flow resistance with a flow property of
less than 220% were judged as "OK." The adhesives of Examples 1-5 received a
judgment of "OK," while those of Comparative Examples 1-4 were all judged as
15 "NG."

3. Adhesive Strength

A film adhesive of 10 x 30 mm² was sandwiched between a copper plate
(30 mm length x 25 mm width x 0.3 mm thickness) and a 50 μm polyimide film
20 and compression bonded at 200°C, 5 N (Newtons) /cm² for 10 seconds to form a
laminate consisting of three layers: copper plate/film adhesive/polyimide film.
The 90° peel strength of this laminate (peel strength between polyimide film and
film adhesive) upon pulling the polyimide film at a speed of 50 mm/min was
measured as the adhesive strength.

25

3. Soldering Heat Resistance

This test was carried out according to the JEDEC standard mentioned
above. First, a 15 x 15 mm² film adhesive was sandwiched between a 0.6-mm
long stainless steel plate and a 125- μm thick polyimide and compression bonded at
30 200°C, 5 N (Newtons)/cm² for 10 seconds to form a laminate consisting of three
layers: stainless steel plate/film adhesive/polyimide film. The laminate was post

cured at 150°C for 2 hours to prepare a test sample. Each of the samples was passed twice through a reflow furnace at 240°C after wet heat aging and samples were given an evaluation of "pass" when no foaming or peeling occurred and an evaluation of "fail" when either or both foaming or peeling occurred.

5 The conditions for the wet heat aging were:

 Level 3: 30°C/50% RH and

 Level 1: 85°C/85% RH.

All of the adhesives of the examples were able to pass the standard for level 3.

10 However, only the adhesive of Example 4 was able to pass level 1. In Example 4, a silica colloid surface-treated with hexamethyldisilazane was used as the inorganic colloid.

3. Elastic Modulus

15 The storage shear elastic modulus G' and loss shear elastic modulus G'' of each sample of the film adhesives was measured using a dynamic viscoelastic analyzer produced by Rheometrics, KK. (Model RDAII). The elastic modulus was the value measured at 250°C upon raising the temperature from 90°C to 300°C at 5°C/min.

 The results of the evaluation are listed in Table 2.

Table 2

	Adhesive properties					
	Flow property	Adhesive strength	Soldering heat resistance		Elastic modulus (250°C, Pa)	
	(%)	(N/cm)	Level 3	Level 1	G'	G''
Example 1	202	12.8	pass	fail	1.04×10^5	1.22×10^4
Example 2	219	13.1	pass	fail	1.44×10^6	2.16×10^4
Example 3	217	15.6	pass	fail	1.15×10^6	2.10×10^4
Example 4	218	14.9	pass	pass	8.59×10^5	7.71×10^3
Example 5	207	17.7	pass	fail	7.49×10^5	1.19×10^4
Comp. Ex. 1	226	25.6	pass	fail	7.03×10^5	1.01×10^4
Comp. Ex. 2	239	8.0	pass	fail	5.43×10^5	9.41×10^3
Comp. Ex. 3	235	13.0	pass	fail	3.91×10^5	7.06×10^3
Comp. Ex. 4	238	14.0	pass	fail	5.11×10^5	6.61×10^3

What Is Claimed Is:

1. A thermosetting adhesive composition comprising:
an adhesive component comprising:
 - 5 (a) a polyethylenic copolymer having at least one epoxy group, and
 - (b) a rosin, characterized in that said rosin has a carboxyl group in the molecule, andan inorganic colloid dispersed in the adhesive component.
- 10 2. The thermosetting adhesive composition of claim 1, wherein the adhesive component further comprises:
 - (c) a thermoplastic polymer having no epoxy groups.
3. The thermosetting adhesive composition of claim 2, wherein the
15 thermoplastic polymer (c) is an ethylene-alkyl (meth)acrylate copolymer.
4. The thermosetting adhesive composition of claim 3, wherein an alkyl group of the ethylene-alkyl (meth)acrylate copolymer has 1 to 4 carbon atoms.
- 20 5. The thermosetting adhesive composition of claim 3, wherein the ethylene-alkyl (meth)acrylate copolymer is derived from a monomer mixture having a polymerization ratio of alkyl (meth)acrylate to ethylene in the range of 50:50 to 5:95.
- 25 6. The thermosetting adhesive composition of claim 1, wherein the polyethylenic copolymer (a) is present in a range of about 40-98% by weight based on total weight of the adhesive component.
7. The thermosetting adhesive composition of claim 2, wherein the
30 thermoplastic polymer (c) is present in a range of about 1-50% by weight based on total weight of the adhesive component.

8. The thermosetting adhesive composition of claim 2, wherein the total amount of the polyethylenic copolymer (a) and thermoplastic polymer (c) is about 60-99% by weight based on total weight of the adhesive component.
- 5 9. The thermosetting adhesive composition of claim 1, wherein the polyethylenic copolymer (a) has a melt flow rate of about 20-1,000 when measured at 190°C according to JIS K6760.
- 10 10. The thermosetting adhesive composition of claim 1, wherein the polyethylenic copolymer (a) is selected from the group consisting of a glycidyl (meth)acrylate and ethylene bipolymer; a glycidyl (meth)acrylate, vinyl acetate, and ethylene terpolymer; and a glycidyl (meth)acrylate, ethylene and alkyl (meth)acrylate terpolymer.
- 15 11. The thermosetting adhesive composition of claim 10, wherein the polyethylenic copolymer (a) is derived from a monomer mixture having a polymerization ratio of glycidyl (meth)acrylate to ethylene in the range of 20:80 to 5:95.
- 20 12. The thermosetting adhesive composition of claim 1, wherein the polyethylenic copolymer (a) contains repeating units comprising glycidyl (meth)acrylate and ethylene in an amount of at least about 75% by weight based on total weight of the polyethylenic copolymer (a).
- 25 13. The thermosetting adhesive composition of claim 1, wherein the rosin (b) has an acid value of about 100-300.
14. The thermosetting adhesive composition of claim 1, wherein the rosin (b) has a softening point of about 50-200°C when measured according to JIS K6730.

30

15. The thermosetting adhesive composition of claim 1, wherein the rosin (b) is present in an amount of about 1-20% by weight based on total weight of the adhesive component.
- 5 16. The thermosetting adhesive composition of claim 1, wherein the inorganic colloid is a silica colloid.
17. The thermosetting adhesive composition of claim 1, wherein the inorganic colloid is present in an amount of about 1-40% by weight based on total weight of the adhesive composition.
- 10
18. An adhesive, wherein a crosslinked structure has been introduced between ethylene units of the polyethylenic copolymer (a) of the thermosetting adhesive composition according to claim 1.
- 15
19. A substrate coated with the adhesive of claim 18.
20. An electronic part comprising the adhesive of claim 18.

INTERNATIONAL SEARCH REPORT

Int. Patent Application No.

PCT/US 99/23499

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C09J11/04 C09J123/08 C08K3/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C09J C08K

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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T	DATABASE WPI Derwent Publications Ltd., London, GB; AN 1999-076686 XP002126414 & JP 10 316955 A (3M), 2 December 1998 (1998-12-02) abstract	1-20
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

Int. Patent Application No
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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